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(71) Applicant : MITSUBISHI MATERIALS CORP
DAINIPPON TORYO CO LTD

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(72) Inventor : MUROUCHI MASAHIKO
HAYASHI TOSHIHARU
NISHIHARA AKIRA
ISHIHARA MASAOKI

(54) CONDUCTIVE FILM-FORMING COMPOSITION AND PRODUCTION OF GLASS PLATE COVERED WITH TRANSPARENT CONDUCTIVE FILM

(57) Abstract:

PURPOSE: To obtain a compsn. capable of forming a glassy transparent conductive film excellent in transparency, electrical conductivity, adhesion and coating film hardness according to a coating method by blending an ITO powder with a solvent, a coupling agent, and a specific metal compd. at specific proportions.

CONSTITUTION: This compsn. comprises 100 pts.wt. tin-contg. indium oxide powder (ITO powder), a solvent, 0.5-5 pts.wt. coupling agent, and 0.2-15 pts.wt. metal compd. selected from among metal salts of org. acids and inorg. acids. This compsn. is applied on a glass plate and fired in an inert or reducing atmosphere at or above 300°C to produce a glass plate covered with a transparent conductive film.

Alternatively, liq. A comprising the ITO powder, solvent and coupling agent may be applied on a glass plate to form a coating film, which is then impregnated with liq. B comprising the metal compd. and solvent, followed by firing. A glass plate covered with a transparent conductive film can be produced by a simple and effective coating method.

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CLAIMS

[Claim(s)]

[Claim 1] the metallic compounds chosen as the indium oxide powder containing tin, the solvent, the coupling agent, and the row from metaled organic acid chloride and the inorganic-acid salt -- a shell -- the constituent for electric conduction film formation of a non-binder -- it is -- the aforementioned indium oxide powder 100 the weight section -- receiving -- the aforementioned coupling agent 0.1 - 5 weight section and the aforementioned metallic compounds Constituent for electric conduction film formation which 0.2 - 15 weight section comes out comparatively, and is characterized by containing.

[Claim 2] It is the aforementioned powder 100 to the indium oxide powder containing tin, a solvent, and a row. As opposed to the weight section 2 liquid type constituent for electric conduction film formation of a non-binder which consists of B liquid which consists of A liquid which consists of a coupling agent of the amount of 0.1 - 5 weight section, and the metallic compounds chosen from metaled organic acid chloride and the inorganic-acid salt and a solvent.

[Claim 3] It is the aforementioned powder 100 about the metallic compounds with which the aforementioned A liquid was chosen from metaled organic acid chloride and the inorganic-acid salt. Constituent for electric conduction film formation according to claim 2 further contained in the amount fewer than 15 weight sections to the weight section.

[Claim 4] The constituent for electric conduction film formation according to claim 1, 2, or 3 which is a compound of the metal with which the aforementioned coupling agent was chosen from the silane system coupling agent, the titanate system coupling agent, and the aluminum NETO system coupling agent, and the aforementioned metallic compounds were chosen from Co, nickel, Pb, In, Zn, aluminum, Fe, Ti, Sn, and Sb.

[Claim 5] The manufacture method of a transparent electric conduction film covering glass plate which applies the constituent for electric conduction film formation according to claim 1 or 4 to a glass plate, and consists of calcinating in inactive [more than 300 **], or a reducing atmosphere.

[Claim 6] The amount of the aforementioned metallic compounds in the paint film after sinking in is the aforementioned powder 100 about B liquid of this constituent for electric conduction film formation to the paint film obtained after applying A liquid of the constituent for electric conduction film formation according to claim 2, 3, or 4 to a glass plate. As opposed to the weight section The manufacture method of a transparent electric conduction film covering glass plate which is infiltrated so that it may become 0.2 - 15 weight section, and consists of calcinating in inactive [more than 300 **], or a reducing atmosphere.

[Claim 7] The manufacture method of the transparent electric conduction film covering glass plate according to claim 5 or 6 which is the compound of the metal with which the aforementioned coupling agent was chosen from the silane system coupling agent, the titanate system coupling agent, and the aluminum NETO system coupling agent, and the aforementioned metallic compounds were chosen from Co, nickel, Pb, In, Zn, aluminum, Fe, Ti, Sn, and Sb.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] this invention relates to the transparent electric conduction film covering glass formed from the constituent for electric conduction film formation which can be used for fields, such as a transparent electrode, an antistatic film, a heat ray reflective film, an electromagnetic wave shield film, a field heating element, and a touch panel, and its constituent for electric conduction film formation.

[0002]

[Description of the Prior Art] The method of forming a transparent electric conduction film is divided roughly into a gaseous-phase method including CVD, the sputtering method, etc., and the applying method. Although a gaseous-phase method is used more widely than before, it is the ***** formation method and a highly efficient transparent electric conduction film can be formed, equipment is expensive, and productivity and the yield are bad and unsuitable for membrane formation of a large area.

[0003] On the other hand, it is a binder solution about a conductive particle. (the solution which consists of a binder and a solvent) It can be made to be able to distribute to inside, it can paint-size, and a substrate can be made to be able to apply and dry and harden the obtained conductive paint, and the applying method which forms a transparent electric-conduction film has few the sizes of a substrate and the limits of formation which form an electric-conduction film, and a facility is easy, is excellent in It is a haze with the applying method. (the degree of overcast) In order to obtain the electric conduction film excellent in low transparency, it is important to distribute a conductive particle nearly completely to the state near a primary particle in a binder solution in the stage of paint-izing. That is, a binder needs to achieve the operation which distributes ITO powder, and the operation which combines ITO powder.

[0004] Although the resin excellent in transparency, such as acrylic resin, polyester resin, and polycarbonate resin, is common as a binder, metal alkoxides, such as an ethyl silicate and its condensate, may be used. indium oxide containing tin by which it is known that the example of representation will obtain the film of low resistance especially although the zinc oxide which contains aluminum or other metals as a dope atom, the tin oxide containing antimony, etc. can be used as a conductive particle (henceforth ITO) it is .

[0005]

[Problem(s) to be Solved by the Invention] In recent years, the improvement in optical property with much more transparent electrode and antistatic film with which highly efficient-ization of a liquid crystal display, a touch panel, a plasma display, an electroluminescence display, or a fluorescence display is used for **** better ** and these, and conductivity has come to be called for. However, even if ITO powder was used for the electric conduction film formed by the applying method as a conductive particle, compared with what was obtained by the gaseous-phase method, it is inferior a haze and in respect of conductivity, and was not able to respond to the above-mentioned request at satisfaction.

[0006] The purpose of this invention is offering the transparent electric conduction film covering glass formed from the constituent for electric conduction film formation which can form the electric conduction film excellent in a haze, conductivity, adhesion, and the film degree of hardness, and its constituent for transparent electric conduction film formation using the applying method which can form an electric conduction film easily.

[0007]

[Means for Solving the Problem] This invention persons repeated examination that the above-mentioned purpose should be attained. consequently, in the conventional conductive coating material used for the applying method which consists of ITO powder, a solvent, and a binder In order that the front face of ITO powder may be covered with an insulating binder and a binder may remain also in the paint film after dryness or printing at the distributed-processing

process of the ITO powder performed to the well of a haze fall, It is covered with a binder, an electronic transition [need / to be direct contacted / between powder] is checked, and the ITO powder in a paint film is conductive improvement. (fall of resistance) It turns out that it bars.

[0008] Therefore, in the conventional conductive coating material which used the binder, if enough ITO powder is distributed in order to give priority to a haze fall, membranous resistance will increase. On the contrary, if priority is given to the fall of resistance, distribution of ITO powder will fall victim and a haze will become high. Therefore, it is difficult to improve a haze and conductivity simultaneously.

[0009] As a result of continuing research further based on such knowledge, even if it used the coupling agent decomposed instead of a binder at the time of baking, it found out that ITO powder could fully be distributed in a paint. However, the bonding strength of ITO powder is insufficient, the adhesion and the film degree of hardness of a transparent electric conduction film which are obtained after baking fall, and just the coupling agent of a haze or conductivity is also still inadequate. Metallic compounds, such as metaled organic acid chloride or an inorganic-acid salt, were used for this point as a sintering acid, it could solve them by infiltrating the solution of these metallic compounds into the paint film which blends these metallic compounds together with the coupling agent into the paint beforehand, or was obtained from ITO powder and the coupling agent, and that the above-mentioned purpose can be attained made it clear.

[0010] Which form of 1 liquid type constituent of the following ** and 2 liquid type constituent of the following ** is sufficient as the constituent for electric conduction film formation of this invention.

** indium oxide powder containing tin (=ITO powder) the metallic compounds chosen as the solvent, the coupling agent, and the row from metaled organic acid chloride and the inorganic-acid salt -- a shell -- the constituent for electric conduction film formation -- it is -- the aforementioned indium oxide powder 100 the weight section -- receiving -- the aforementioned coupling agent 0.1 - 5 weight section and the aforementioned metallic compounds Constituent for electric conduction film formation of the non-binder which 0.2 - 15 weight section comes out comparatively, and is characterized by containing.

[0011] ** It is the aforementioned powder 100 to ITO powder, a solvent, and a row. As opposed to the weight section 2 liquid type constituent for electric conduction film formation of a non-binder which consists of B liquid which consists of A liquid which consists of a coupling agent of the amount of 0.1 - 5 weight section, and the metallic compounds chosen from metaled organic acid chloride and the inorganic-acid salt and a solvent. However, A liquid is the aforementioned powder 100 about the above-mentioned metallic compounds. You may contain further in the amount fewer than 15 weight sections to the weight section. That is, you may make some above-mentioned metallic compounds exist in A liquid.

[0012] If it is in a suitable mode, the aforementioned coupling agent is chosen from a silane system coupling agent, a titanate system coupling agent, and an aluminum NETO system coupling agent, and the aforementioned metallic compounds are compounds of the metal chosen from Co, nickel, Pb, In, Zn, aluminum, Fe, Ti, Sn, and Sb.

[0013] The 1 liquid type constituent for electric conduction film formation of the above-mentioned ** can form a transparent electric conduction film on a glass plate by applying this to a glass plate and calcinating in inactive [more than 300 **], or a reducing atmosphere.

[0014] The 2 liquid type constituent for electric conduction film formation of the above-mentioned ** is the aforementioned powder 100 to the paint film obtained after applying the A liquid to a glass plate. As opposed to the weight section A transparent electric conduction film can be formed on a glass plate by infiltrating B liquid containing the aforementioned metallic compounds of the amount of 0.2 - 15 weight section, and calcinating in inactive [more than 300 **], or a reducing atmosphere. In addition, when A liquid has already contained the aforementioned metallic compounds, for the amount of sinking in of B liquid, the aforementioned metallic compounds in the paint film after sinking in are the aforementioned powder 100 comparatively. As opposed to the weight section It is made to become 0.2 - 15 weight section.

[0015] In addition, the 2 liquid type constituent for electric conduction film formation can mix A liquid and B liquid before an application, can apply and calcinate them like the 1 above-mentioned liquid type constituent for electric conduction film formation, and can also form a transparent electric conduction film on a glass plate.

[0016] It has the structure sintered with inorganic metallic compounds, such as a metallic oxide to which ITO powder also generated the transparent electric conduction film obtained by which method by disassembly of the metallic compounds used as a coupling agent and a sintering acid.

[0017]

[Function] Commercial elegance may be used for the ITO powder used by this invention, or it is a well-known method

(for example, neutralize the acid solution of the chloride of tin and an indium with alkali, tin / indium hydroxide is made to coprecipitate, and this coprecipitate is calcinated). It can also manufacture. ITO powder (In+Sn), Since the thing of the range of 1 - 15 atom % is especially low resistance, its content of Sn to the total quantity is desirable. When Sn content separates from this range, it is resistance of the ITO powder itself. (volume-resistivity value) There is an inclination which becomes high. Moreover, the first [an average of] particle diameter of ITO powder is 0.5 so that the transparency of the formed film may not be checked. It is especially 0.2 below mum. It is desirable that it is below mum.

[0018] Since polar groups, such as OH basis, exist in the front face of ITO powder and it consists of a moreover very detailed particle, surface activity is high. Therefore, in order very to be easy to condense ITO powder and to make it distribute in a solvent, in the dispersant or the surfactant, it became clear that the pyrolysis object which will have a bad influence on conductivity at the time of baking even if it is difficult to distribute ITO powder completely and is able to distribute arises.

[0019] In this invention, ITO powder is distributed in a solvent using a coupling agent. It is desirable to use one sort chosen from the silane system coupling agent, the titanate system coupling agent, and the aluminum NETO system coupling agent as an usable coupling agent or two sorts or more by this invention. The titanate system coupling agent which has the silane system coupling agent which has the alkyl group or phenyl group of carbon numbers 1-8, the titanate system coupling agent which has the alkylate machine of carbon numbers 1-18, an alkyl phosphite machine, or an alkyl PAIRO phosphate machine as an example of these coupling agents, and the aluminum NETO system coupling agent which has the aceto alkoxy group in a row are mentioned as a typical thing.

[0020] As the example of the coupling agent which can be used by this invention Methyl triethoxysilane, n-propyltrimethoxysilane, isobutyl trimethoxysilane, The silane system coupling agent which has the alkyl group of the carbon numbers 1-8, such as octyl triethoxysilane; Phenyl trimethoxysilane, The silane system coupling agent which has phenyl groups, such as phenyl triethoxysilane and diphenyl diethoxysilane; Isopropylisostearoyl titanate, The titanate system coupling agent which has the alkylate machine of the carbon numbers 1-18, such as isopropyl TORIOKUCHI roil titanate; tetrapod isopropyl screw (dioctyl phosphite) Titanate, Tetrapod octyl screw (didodecyl phosphite) The titanate system coupling agent which has alkyl phosphite machines, such as titanate; screw (dioctylpyrophosphate) Oxy-acetate titanate, Isopropyl tris (dioctylpyrophosphate) The titanate system coupling agent which has alkyl PAIRO phosphate machines, such as titanate; [Aceto ethyl aluminum JIISOPUROPIRETO,] The aluminum NETO system aluminate coupling agent which has the aceto alkoxy groups, such as aceto octyl aluminum JIISOPUROPIRETO, is mentioned.

[0021] These coupling agents are the high polar groups of the compatibility over ITO powder. (an example, alkoxy group) High basis of the compatibility over a solvent (an example, an alkyl group, phenyl group) It has. As a result of the polar group of a coupling agent combining with the polar group of an ITO powder front face and adsorbing a powder front face moderately in a coupling agent, powdered condensation is controlled, and when another basis of a coupling agent shows compatibility to a solvent simultaneously, that whose dispersibility in the inside of the solvent of ITO powder improves is conjectured. Moreover, since a coupling agent is an organometallic compound, it is pyrolyzed during baking, changes to inorganic metallic compounds, and contributes also to sintering of ITO powder. However, by the coupling-agent independent, as mentioned above, since the combination between the particles of ITO powder and between the glass of this particle and a base is not enough, the sintering acid mentioned later independently is also used together.

[0022] the amount of the coupling agent used -- ITO powder 100 Amount to the weight section 0.1 - 5 weight section -- desirable -- It is the range of 0.5 - 3 weight section. The amount of a coupling agent is 0.1. Distributing [of ITO powder] becomes being under the weight section inadequate, and optical properties, such as a haze, fall. Moreover, if the amount of a coupling agent exceeds 5 weight sections, covering to ITO powder will increase and conductivity will become bad.

[0023] The metallic compounds used as a sintering acid by this invention are chosen from metaled organic acid chloride and an inorganic-acid salt, and these one sort or two sorts or more can be used for them. These metallic compounds change with baking to inorganic metallic compounds, and combine between the particles of ITO powder, and between the glass of this particle and a base, and adhesion contributes them to formation of the good transparent electric conduction film of a high degree of hardness.

[0024] The metal which is excellent in the transparency after converting into an inorganic oxide as these metallic compounds, and does not block a membranous haze is desirable, and it is desirable to use the compound of the metal specifically chosen from Co, nickel, Pb, In, Zn, aluminum, Fe, Ti, Sn, and Sb.

[0025] as the example of metallic compounds useful as a sintering acid -- the aliphatic series of the metaled carbon numbers 1-20, alicyclic, and aromatic carboxylate s (for example, an octylic acid indium, octylic acid zinc, butanoic acid tin, naphthenic-acid cobalt, benzoic-acid lead, etc.) a row -- inorganic-acid salts, such as a nitrate, a sulfate, and phosphate s (for example, a nitric-acid indium, a cobalt nitrate; a lead nitrate, etc.) etc. -- it is mentioned as a typical thing

[0026] the amount of the metallic compounds of a sintering acid -- ITO powder 100 it is an amount to the weight section -- 0.2 - 15 weight section -- desirable -- It is the range of 0.5 - 10 weight section. The amount of these metallic compounds is 0.2. The degree of sintering of the ITO powder at the time of baking becomes being under the weight section inadequate, and film properties, such as conductivity and adhesion, fall. On the other hand, if the amount of these metallic compounds exceeds 15 weight sections, a metal will appear in the paint film after baking, a haze will become high, and adhesion will fall.

[0027] As a solvent which distributes ITO powder, water etc. is mentioned to amides rows, such as hydrocarbons [, such as ketones, such as alcohols, such as a methanol, ethanol, an isopropanol, and a butanol an acetone a methyl ethyl ketone diacetone alcohol, a cyclohexanone, and an isophorone, toluene, a xylene, a hexane, and a cyclohexane,], N,N-dimethylformamide, N, and N-dimethylacetamide. According to these kinds, a solvent chooses one sort or two sorts or more, and is used so that the coupling agent to be used may dissolve and the metallic compounds of a sintering acid may distribute to the dissolution or stability. Especially the amount of a solvent should just be an amount from which the constituent of viscosity which was not restricted but fitted the application is obtained. Usually, the amount used from which the solid content of a constituent serves as 5 - 60% of the weight of a range is suitable.

[0028] Although the constituent for electric conduction film formation is prepared using the metallic compounds of the above-mentioned ITO powder, a solvent, a coupling agent, and a sintering acid, in this invention, the constituent for electric conduction film formation of two kinds of forms, 1 liquid type and a 2 liquid type, is possible.

[0029] The constituent for electric conduction film formation of a 1 liquid type this invention can be prepared by distributing ITO powder in the solution which the metallic compounds of a coupling agent and a sintering acid dissolved or distributed. Each component can use one sort or two sorts or more. Mixture can be carried out by the arbitrary meanses conventionally used for manufacture of a paint. This constituent can also be made to contain arbitrary addition components other than the above further by request. Although a surfactant, a leveling agent, etc. are mentioned as the example of such an addition component, 5 or less % of the weight of the solid content of the constituent for electric conduction film formation of adding these so much is usually desirable preferably.

[0030] the obtained constituent for electric conduction film formation -- the glass plate of a substrate -- desirable -- an alkali-free-glass board -- applying -- more than 300 ** -- desirable -- If it calcinates in inactive [of 350 - 550 **], or a reducing atmosphere, a transparent electric conduction film will be formed. What is necessary is just to enforce the method of application by conventional methods, such as a spin coat, a roll coat, a spray coat, and a flow coat. The examples of a firing environments are inert gas atmosphere, such as nitrogen and an argon, or a reducing gas atmosphere which consists of mixed gas of this inert gas and hydrogen. Especially a firing time is usual although not restricted. It is the range of 0.5 - 2 hours. Application thickness is 0.05-5.0 at dryness thickness. The range of mum is desirable.

[0031] A liquid which mixed ITO powder, the solvent, and the coupling agent in the constituent for electric conduction film formation of a 2 liquid type this invention (distributed liquid which ITO powder distributed in the solvent which the coupling agent dissolved) B liquid which mixed the metallic compounds and the solvent of a sintering acid (liquid which metallic compounds dissolved or distributed in the solvent) It prepares.

[0032] As mentioned above, you may blend some metallic compounds of a sintering acid into A liquid by request. Therefore, the content of metallic compounds can also use the constituent for electric conduction film formation of a comparatively few 1 above-mentioned liquid type this invention as A liquid.

[0033] This A liquid is applied on the glass plate of a substrate, and is dried if needed. Then, B liquid is infiltrated into the obtained paint film. This sinking in can carry out the glass plate which applied B liquid or applied A liquid by being immersed into B liquid. The applying method is the same as that of the above, and is good. The amount of sinking in of B liquid to a paint film is the ITO powder 100 in a paint film like a 1 liquid type case. The amounts of the metallic compounds in B liquid to the weight section are 0.2 - 15 weight section and an amount which serves as 0.5 - 10 weight section preferably. After sinking [of B liquid] in calcinates on the same conditions as the above.

[0034] As mentioned above, it can also be mixed and used before applying 2 liquid type A liquid and B liquid of the constituent for electric conduction film formation. in this case, the mixing ratio of A liquid and B liquid -- a rate -- ITO powder 100 after mixture Amount of the metallic compounds to the weight section It considers as a ratio which

becomes within the limits of 0.2 - 15 weight section. Since the 1 liquid type constituent for electric conduction film formation mentioned above is obtained by this mixture, this is applied like the 1 liquid type constituent for electric conduction film formation, and is calcinated by it.

[0035] In the paint film before baking, when which constituent for electric conduction film formation of 1 liquid type and a 2 liquid type is used, when a coupling agent sticks to an ITO powder front face, ITO powder distributes to sufficient grade for the reduction in a haze, and the metallic compounds of a sintering acid exist in the gap between this dispersed ITO powder. And it decomposes, ITO powder welds a coupling agent and a sintering acid through the inorganic metallic compounds generated by disassembly of these compounds, and sintering of ITO powder is performed by baking. That is, when between the particles of ITO powder and between ITO powder and glass bases join together with the inorganic metallic compounds which are decomposition products of a coupling agent and a sintering acid, the transparent electric conduction film which stuck to the base and was united with it is formed on a glass plate. In addition, in the inorganic metallic compounds generated by decomposition, the organic substance may remain somewhat in the range in which conductivity is not reduced remarkably.

[0036] By carrying out burning temperature to more than 300 **, move diffusion of the oxygen atom especially in a grain boundary is promoted, and combination between ITO powder can be strengthened using the crystal growth accompanying it. Therefore, the transparent electric conduction film covering glass plate conductivity, adhesion, and whose film degree of hardness improved remarkably is obtained, keeping a haze low.

[0037]

[Example] Next, an example explains this invention concretely. In addition, the ITO powder used in the example is all. (In+Sn) Sn content to the total quantity is the powder which is five atom % and 0.05 micrometers of first [an average of] particle diameters.

[0038] (Example 1) this example illustrates manufacture of the transparent electric conduction film covering glass plate using the 1 liquid type constituent for electric conduction film formation concerning this invention.

[0039] Metallic compounds of the kind which shows ITO powder in Table 1 and the solvent of a rate, a coupling agent, and a sintering acid. (Total quantity =100 g of the above component) It puts into the container of 250 cc and is a diameter. Zirconia beads of 0.3 - 0.6 mm (micro hiker and SHOWA SHELL SEKIYU make) The 1 liquid type constituent for electric conduction film formation was obtained by adding 100g, mixing with a paint shaker for 3 hours, and distributing ITO powder. After removing a bead, visual observation estimated the distributed state of the ITO powder of a constituent.

[0040] In this way, glass plate which made each prepared constituent for electric conduction film formation incline (2mm in thickness, haze 0.0 %) It applied by the flow coat method, it calcinated in the temperature and atmosphere which were indicated to Table 1 for 1 hour, and the transparent electric conduction film was formed on the glass plate. ITO powder 100 in the paint film before baking The amount of the coupling agent to the weight section and metallic compounds is also shown in Table 1.

[0041] It is a four point probe method about the surface-electrical-resistance value of the obtained transparent electric conduction film. (RORESUTA AP: Mitsubishi Petrochemical) It is a hazemeter (HGM-3D:SUGA testing machine). about a haze. It measured. Moreover, it is 1mm/mm about adhesion from a SEM cross-section photograph in thickness. The base eye cross-cut cellophane tape exfoliating method (100 grids) It asked for the film degree of hardness by the pencil degree-of-hardness method. These measurement results are also shown in Table 1.

[0042] a comparison sake -- composition of the constituent for electric conduction film formation -- this invention -- being out of range -- or -- the example of comparison with baking conditions out of range [this invention] -- the experiment was also conducted The test condition and test result are also collectively shown in Table 1.

[0043] In addition, the meaning of the sign of the solvent used in Table 1, a coupling agent, an organometallic compound, and inorganic metallic compounds is as follows, and the ratio in a parenthesis is a weight ratio.

1) Solvent A:xylene B : a xylene/diacetone alcohol. (70/30) C:xylene / diacetone alcohol / acetylacetone (65/30/5) 2 coupling-agent D: -- screw (dioctylpyrophosphate) Oxy-acetate titanate E:tetrapod octyl screw (JITORI desyl phosphite) Titanate F: Isopropylstearoyl-titanate G: Aceto staryl aluminum JIISOPUROPIRETO H:octyl trimethoxysilane I : Diphenyl dimethoxysilane J:D+E 3 (50/50)-organometallic-compound K:octylic acid In / naphthenic acid Fe L : Octylic acid In / octylic acid Sn (95/5) M : Octylic acid In / octylic acid Sb (95/5) N: (95/5) Octylic acid In / octylic acid aluminum / octylic acid Ti 4 (95/3/2) Inorganic metallic compounds P: Nitric-acid In / nitric acid Co 5 (80/20) Acrylic resin LR 980 (resin solid-content 38wt%) made from binder resin Mitsubishi rayon .

[0044]

[Table 1]

| 項目 試験 No | ITO wt% | 溶媒 wt% | カーバイド 金屬化合物 wt% | 塗膜組成(粉末 100 部分割合) | | 焼成条件 温度 ℃ | 透明度 % 雾 気 | ITO 粉末 分散 状態 μm | ヘイ ズ % 硬度 | 鉛筆 密着性 △/□ | 透明導電膜の特性 表面抵抗値 Ω/□ |
|----------------|---|-----------|-----------------------|----------------------|-----------|-----------------|--------------------|-----------------------------|--------------------|------------------|--------------------------|
| | | | | 種類 wt% | 種類 wt% | | | | | | |
| 実 施 例 | 1 20.0 A 77.9 D 0.10 オクチル酸In 2.0 0.5 10.0 450 N ₂ /H ₂ (85/5) 良好 1.0 0.4 5 H 100/100 5.0×10 ² | | | | | | | | | | |
| | 2 20.0 A 77.9 D 0.10 オクチル酸In 2.0 0.5 10.0 450 N ₂ /H ₂ (85/5) 良好 1.0 0.4 5 H 100/100 1.5×10 ¹ | | | | | | | | | | |
| | 3 20.0 A 77.4 D 0.60 オクチル酸In 2.0 3.0 10.0 450 N ₂ /H ₂ (85/5) 良好 1.0 0.3 8 H 100/100 4.5×10 ¹ | | | | | | | | | | |
| | 4 20.0 A 79.8 D 0.10 オクチル酸In 0.1 0.5 0.5 950 N ₂ /H ₂ (85/5) 良好 1.0 0.5 4 H 100/100 3.0×10 ¹ | | | | | | | | | | |
| | 5 20.0 B 77.8 E 0.20 オクチル酸Zn 2.0 1.0 10.0 450 N ₂ /H ₂ (85/5) 良好 1.0 0.6 5 H 100/100 5.5×10 ¹ | | | | | | | | | | |
| | 6 20.0 B 77.8 E 0.20 オクチル酸Ni 2.0 1.0 10.0 450 N ₂ /H ₂ (85/5) 良好 1.0 0.6 4 H 100/100 6.3×10 ¹ | | | | | | | | | | |
| 実 施 例 | 7 20.0 C 77.8 F 0.20 K 2.0 1.0 10.0 550 N ₂ /H ₂ (85/5) 良好 1.0 0.8 5 H 100/100 4.5×10 ¹ | | | | | | | | | | |
| | 8 20.0 C 77.8 F 0.20 L 2.0 1.0 10.0 450 N ₂ /H ₂ (85/5) 良好 1.0 0.5 6 H 100/100 1.2×10 ¹ | | | | | | | | | | |
| | 9 20.0 C 77.8 G 0.20 M 2.0 1.0 10.0 450 N ₂ /H ₂ (85/5) 良好 1.0 0.5 7 H 100/100 1.4×10 ¹ | | | | | | | | | | |
| | 10 20.0 C 77.8 H 0.20 N 2.0 1.0 10.0 450 N ₂ /H ₂ (85/5) 良好 1.0 0.6 6 H 100/100 3.5×10 ¹ | | | | | | | | | | |
| | 11 20.0 C 77.8 I 0.20 硝酸In 2.0 1.0 10.0 450 N ₂ /H ₂ (85/5) 良好 1.0 0.4 5 H 100/100 1.3×10 ¹ | | | | | | | | | | |
| | 12 20.0 C 77.8 J 0.20 硝酸Pb 2.0 1.0 10.0 450 N ₂ /H ₂ (85/5) 良好 1.0 0.5 6 H 100/100 6.0×10 ¹ | | | | | | | | | | |
| 実 例 | 13 20.0 C 77.8 P 0.20 硝酸In 2.0 1.0 10.0 450 N ₂ /H ₂ (85/5) 良好 1.0 0.6 4 H 100/100 1.5×10 ¹ | | | | | | | | | | |
| | 14 20.0 C 77.8 J 0.20 オクチル酸In 1.0 1.0 10.0 450 N ₂ /H ₂ (85/5) 良好 1.0 0.5 5 H 100/100 1.3×10 ¹ | | | | | | | | | | |
| | 15 20.0 A 77.8 D 0.20 オクチル酸In 2.0 1.0 10.0 200 N ₂ /H ₂ (85/5) 良好 1.0 1.2 H 25/100 4.0×10 ³ | | | | | | | | | | |
| | 16 20.0 A 79.8 D 0.20 — — 1.0 450 N ₂ /H ₂ (85/5) 良好 1.0 1.6 2 H 30/100 5.0×10 ³ | | | | | | | | | | |
| | 17 20.0 A 69.8 D 0.20 オクチル酸In 10.0 1.0 50.0 450 N ₂ /H ₂ (85/5) 良好 1.0 50.0 H 20/100 5.0×10 ² | | | | | | | | | | |
| | 18 20.0 A 78.0 — — オクチル酸In 2.0 10.0 450 N ₂ /H ₂ (85/5) 不良 — — — — | | | | | | | | | | |
| 比較 例 | 19 20.0 A 76.0 D 3.0 オクチル酸In 1.0 15.0 5.0 450 N ₂ /H ₂ (85/5) 良好 1.0 0.8 5 H 100/100 8.0×10 ⁴ | | | | | | | | | | |
| | 20 20.0 B 70.8 オクチル酸In 9.2% — 150 大気 良好 1.0 2.5 H 60/100 8.0×10 ³ | | | | | | | | | | |

溶媒-A:キシレン; B:オクチルアルコール/アセトニル/ジメチルホスファイト
 カップリング剤-D:ビス(ジオクチルハイドロホスフェート)オキシアセテートチタネット; E:トラオクチルチタネット; G:アセトステアリアルミニウムジイソプロピレート;
 チタネット; F:イソブロピルトリソステアリルチタネット; I:ジフェニルジメトキシシラン; J:ジメチルトリメトキシシラン; K:オクチル酸In/オクチル酸Sn(95/5); L:オクチル酸In/オクチル酸Sn(95/5); M:硝酸In/硝酸Sn(80/20);
 N:オクチル酸In/オクチル酸Al/オクチル酸Ti(95/3/2); P:硝酸In/硝酸Sn(80/20)

[0045] As shown in Table 1, this invention is followed, and at an example, they are less than [haze 1%] and the surface-electrical-resistance values 101-102. omega/** (most is 101 omega / ** base) Adhesion The electric conduction film which was excellent in adhesion and the degree of hardness with 100/100, the low haze more than of pencil degree-of-hardness 4H, and low resistance was able to be formed. On the other hand, burning temperature is under 300 **, or it is transparency at the example of comparison with the amount of a coupling agent or a sintering acid out of range. (haze) Each of conductivity, adhesion, and film degrees of hardness fell. Moreover, all of a haze, conductivity, and adhesion were inferior also in the transparent electric conduction film obtained using the binder resin by the conventional method.

[0046] (Example 2) In this example, manufacture of the transparent electric conduction film covering glass plate using

the 2 liquid type constituent for electric conduction film formation concerning this invention and this constituent is illustrated.

[0047] The solvent and coupling agent of the kind which shows ITO powder to the column of A liquid of Table 2, and a rate. (Total quantity =100 g of the above component) It puts into the container of 250 cc and they are the zirconia beads of a diameter 0.3 - 0.6 mm. (micro hiker and SHOWA SHELL SEKIYU make) By adding 100 g, mixing with a paint shaker for 3 hours, and distributing ITO powder, it is the ITO powder distribution liquid for an application. (A liquid) It obtained. Moreover, the ITO distribution liquid obtained by examination No.4 of an example 1 was also used as A liquid. After removing a bead, viewing estimated the distributed state of the ITO powder of this A liquid.

[0048] It is a constituent for sinking in by making a solvent dissolve or distribute organic [of a sintering acid], and/or inorganic metallic compounds independently at the kind and rate which are shown in the column of B liquid of Table 2. (B liquid) It prepared.

[0049] Glass plate which made the A above-mentioned liquid each incline (2mm in thickness, haze 0.0 %) After applying by the flow coat method and drying a paint film by air-drying, on the obtained paint film, B liquid was again applied by the flow coat method, the paint film was infiltrated, and it was made to dry. ITO powder 100 in the dry paint film after sinking in The amount of the coupling agent to the weight section and metallic compounds is shown in Table 2. Then, it calcinated in the temperature and atmosphere which were indicated to Table 2 for 1 hour, and the transparent electric conduction film was formed on the glass plate. The result which measured the surface-electrical-resistance value, the haze, the thickness, the adhesion, and the degree of hardness of the obtained electric conduction film like the example 1 is also collectively shown in Table 2.

[0050]

[Table 2]

| 項目 | A液の組成 | | | B液の組成 | | | 塗膜組成 (ITO 粉末100重量部 粉末の重量部) | | | 焼成条件 | | | 導電膜の特性 | | | | | | |
|----|---------------|------------------------|----------------------------|--------------------------|------|------|----------------------------------|-----------|-----|---------------------------------------|------|---------|---------|---------------------------------------|-----------------------------|---------------|--------------|---------|---------------------|
| | ITO wt% | 溶媒 ¹ wt% | カッカジケ類 ² wt% | 金属化合物 種類 ³ | wt% | 種類 | wt% | カッカジ 剤 | wt% | かがん 剤 | wt% | 温度 ℃ | 雰囲 気 | 膜厚 μm | ハース 強度 % ⁴ | 鉛筆 硬度 H | 表面抵抗値 Ω/□ | | |
| 1 | 20.0 | A | 77.9 | D | 0.10 | 良好 | カク酸In | 20.0 | A | 80.0 | 0.5 | 7.0 | 450 | N ₂ (100) | 1.0 | 0.5 | 5 H | 100/100 | 5.0×10 ² |
| 2 | 20.0 | A | 77.9 | D | 0.10 | 良好 | カク酸In | 20.0 | A | 80.0 | 0.5 | 7.0 | 450 | N ₂ /H ₂ (95/5) | 1.0 | 0.5 | 4 H | 100/100 | 1.5×10 ¹ |
| 3 | 20.0 | A | 79.4 | D | 0.60 | 良好 | カク酸In | 20.0 | A | 80.0 | 3.0 | 7.0 | 450 | N ₂ /H ₂ (95/5) | 1.0 | 0.5 | 8 H | 100/100 | 4.5×10 ¹ |
| 4 | 20.0 | A | 79.4 | D | 0.10 | 良好 | カク酸In | 5.0 | A | 95.0 | 0.5 | 0.5 | 350 | N ₂ /H ₂ (95/5) | 1.0 | 0.7 | 5 H | 100/100 | 3.0×10 ¹ |
| 5 | 20.0 | B | 77.8 | E | 0.20 | 良好 | カク酸Ni | 20.0 | B | 80.0 | 1.0 | 7.0 | 450 | N ₂ /H ₂ (95/5) | 1.0 | 0.6 | 5 H | 100/100 | 5.5×10 ¹ |
| 6 | 20.0 | B | 77.8 | E | 0.20 | 良好 | カク酸Zn | 20.0 | B | 80.0 | 1.0 | 7.0 | 450 | N ₂ /H ₂ (95/5) | 1.0 | 0.6 | 5 H | 100/100 | 6.3×10 ¹ |
| 7 | 20.0 | C | 77.8 | F | 0.20 | 良好 | K | 20.0 | B | 80.0 | 1.0 | 7.0 | 550 | N ₂ /H ₂ (95/5) | 1.0 | 0.7 | 6 H | 100/100 | 4.5×10 ¹ |
| 8 | 20.0 | C | 77.8 | G | 0.20 | 良好 | L | 20.0 | B | 80.0 | 1.0 | 7.0 | 450 | N ₂ /H ₂ (95/5) | 1.0 | 0.7 | 7 H | 100/100 | 1.2×10 ¹ |
| 9 | 20.0 | C | 77.8 | H | 0.20 | 良好 | M | 20.0 | B | 80.0 | 1.0 | 7.0 | 450 | N ₂ /H ₂ (95/5) | 1.0 | 0.8 | 7 H | 100/100 | 1.4×10 ¹ |
| 10 | 20.0 | C | 77.8 | I | 0.20 | 良好 | N | 20.0 | A | 80.0 | 1.0 | 7.0 | 450 | N ₂ /H ₂ (95/5) | 1.0 | 0.7 | 6 H | 100/100 | 3.5×10 ¹ |
| 11 | 20.0 | C | 77.8 | J | 0.20 | 良好 | 硝酸In | 30.0 | 水 | 70.0 | 1.0 | 1.0 | 450 | N ₂ /H ₂ (95/5) | 1.0 | 0.5 | 7 H | 100/100 | 2.5×10 ¹ |
| 12 | 20.0 | C | 77.8 | K | 0.20 | 良好 | 硝酸Pb | 30.0 | 水 | 70.0 | 1.0 | 1.0 | 450 | N ₂ /H ₂ (95/5) | 1.0 | 0.6 | 6 H | 100/100 | 4.3×10 ¹ |
| 13 | 20.0 | C | 77.8 | J | 0.20 | 良好 | P | 30.0 | 水 | 70.0 | 1.0 | 1.0 | 450 | N ₂ /H ₂ (95/5) | 1.0 | 0.8 | 5 H | 100/100 | 3.0×10 ¹ |
| 14 | 20.0 | C | 77.8 | J | 0.20 | 良好 | カク酸In | 5.0 | C | 94.0 | 1.0 | 0.6 | 450 | N ₂ /H ₂ (95/5) | 1.0 | 0.9 | 4 H | 100/100 | 1.5×10 ¹ |
| 15 | 表1の試験No.4の組成物 | 良好 | カク酸In | 20.0 | A | 80.0 | 0.5 | 0.5 | 450 | N ₂ /H ₂ (95/5) | 1.0 | 0.3 | 8 H | 100/100 | 1.3×10 ¹ | | | | |
| 16 | 表1の試験No.4の組成物 | 良好 | L | 20.0 | A | 80.0 | 0.5 | 0.5 | 450 | N ₂ /H ₂ (95/5) | 1.0 | 0.4 | 7 H | 100/100 | 1.5×10 ¹ | | | | |
| 17 | 表1の試験No.4の組成物 | 良好 | 硝酸In | 30.0 | 水 | 70.0 | 0.5 | 1.5 | 450 | N ₂ /H ₂ (95/5) | 1.0 | 0.4 | 7 H | 100/100 | 1.3×10 ¹ | | | | |
| 18 | 20.0 | A | 80.0 | — | — | 不良 | — | — | — | — | — | — | — | — | — | — | — | | |
| 19 | 20.0 | A | 77.0 | D | 3.0 | 良好 | — | — | — | — | 15.0 | — | 450 | N ₂ /H ₂ (95/5) | 1.0 | 0.8 | 5 H | 100/100 | 9.0×10 ⁴ |
| 20 | 20.0 | A | 77.0 | D | 3.0 | 良好 | カク酸In | 20.0 | A | 80.0 | 15.0 | 7.0 | 450 | N ₂ /H ₂ (95/5) | 1.0 | 1.6 | 5 H | 100/100 | 5.0×10 ⁴ |
| 21 | 表1の試験No.4の組成物 | 良好 | カク酸In | 50.0 | C | 50.0 | 0.5 | 27.5 | 450 | N ₂ /H ₂ (95/5) | 2.0 | 60.5 | H B | 20/100 | 4.0×10 ⁴ | | | | |

(注) 溶媒、カッカジケ類、有機金属化合物、無機金属化合物の記号の意味は、実施例1と同じ。

[0051] In the example which followed this invention as shown in Table 2 The transparent electric conduction film excellent in both conductivity adhesion transparency and the degree of hardness which considered as the 2 liquid type constituent for electric conduction film formation, and was equipped with the performance which matches in the case of 1 liquid type constituent of an example 1 also by the film formation method of infiltrating B liquid which contains the metallic compounds of a sintering acid in the paint film obtained from ITO powder and A liquid containing a coupling-agent component, and calcinating it was able to be obtained.

[0052]

[Effect of the Invention] The constituent for electric conduction film formation of this invention is the conventional constituent for electric conduction film formation which used the binder. (conductive coating material) It can compare and the glassy transparent electric conduction film excellent in both transparency conductivity adhesion and the paint film degree of hardness can be formed. Consequently, it is 0.05-5.0 by the simple and efficient method of the applying method. It is the thickness of mum. surface-electrical-resistance value 101-103 omega / ** base -- desirable -- 101-102 omega / ** base -- It is 101 still more preferably. omega / ** base, and a haze preferably 2% or less 1% or less, Adhesion (1mm/mm base eye cross-cut Scotch tape exfoliation) 100/100 and a pencil degree of hardness can manufacture preferably the transparent electric conduction film covering glass plate which shows the outstanding property more than of 4H 95/100 or more.

[Translation done.]